AQUEOUS NANOPARTICLE CERAMIC AGGLOMERATE DISPERSION FOR FORMING INK-ABSORBING LAYER OF INK-JET RECORDING MEDIUM

The present invention relates to an aqueous nanoparticle ceramic agglomerate dispersion which is suitable for ink-

5   absorbing layers on ink-jet recording media and which facilitates printing of sharp and clear images on the ink-jet recording media.

Description of the Related Art
A typical conventional ink-jet recording medium includes a

10   substrate having a thickness of 100 to 300 μm, such as paper or a polyethylene film, an ink-absorbing layer having a thickness of 30 to 200 μm formed thereon by coating, and a protective layer having a thickness of 1 to 10 μm composed of a water-soluble resin or the like, which is

15   formed on the ink-absorbing layer by spraying.

In general, the ink-absorbing layer of the ink-jet recording medium is formed as follows. Nanoparticle ceramic agglomerates, such as a powdered silicon oxide (hereinafter referred to as SiO_2) agglomerate and a powdered aluminum

20   oxide (hereinafter referred to as Al_2O_3) agglomerate are added to deionized water to form an aqueous nanoparticle ceramic agglomerate dispersion so that the dispersion has a viscosity suitable for coating of 10 to 200 mPa·s. To the dispersion, for example, a cationic polymer, ethanol,

25   propanol, ethyl acetate, polyvinyl alcohol, and boric acid are added to prepare a coating. The coating is applied onto the substrate surface and is dried.

The above raw materials used for the aqueous nanoparticle ceramic agglomerate dispersion are generally prepared by a

30   vapor phase synthetic method using $SiCl_4$ and $AlCl_3$ in the presence of hydrogen and oxygen, for example, from a burner. The resulting nanoparticle ceramic powder has an extremely small average diameter of 7 to 40 nm. Thus, ceramic particles inevitably interact with each other and

35   readily agglomerate. Even when this nanoparticle ceramic

powder is added to deionized water after disintegration in a ball mill, the nanoparticle ceramic powder is present as a ceramic powder agglomerate having an average diameter of 1 to 30 μm.

5 In the printing of images onto the ink-jet recording medium, fine ink droplets discharged through dot nozzles of an ink-jet printer are absorbed into the ink-absorbing layer. In color printing, such a process is repeated several times using inks of different colors.

10 With trends toward higher performance in ink-jet printers, the size of the ink droplets discharged from the ink-jet printers has been reduced to 20 μm or less. When this ink is discharged onto the above conventional ink-jet recording medium, the ink droplets flow locally in the ink-absorbing 15 layer and result in bleeding. As a result, printed images are not clear, regardless of how ultrafine the ink droplets are.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an 20 aqueous nanoparticle ceramic agglomerate dispersion which is suitable for ink-absorbing layers on ink-jet recording media and which facilitates printing of sharp and clear images onto the ink-jet recording media.

The present inventors have researched aqueous nanoparticle 25 ceramic agglomerate dispersions for ink-absorbing layers so that the ink-absorbing layer can hold ultrafine ink droplets discharged from an ink-jet printer at the discharged positions, and have reached the following conclusions.

30 a) In a conventional aqueous nanoparticle ceramic agglomerate dispersion, the nanoparticle ceramic agglomerate has an average diameter of 1 to 30 μm according to measurements by a laser diffraction particle size distribution measurement apparatus. The

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size distribution curve determined according to the
results of the measurement is shown in Fig. 2. The ratio
of the peak width at a position having a height which is
half the maximum height of the curve (hereinafter

5   referred to as the half width) to the maximum height is
1 to 1.5. Such a ratio indicates that the nanoparticle
ceramic agglomerate is relatively rough and sizes
thereof are not uniform. That is, the size uniformity of
the agglomerates is inadequate. In an auxiliary

10   insulating layer containing such nanoparticle ceramic
agglomerates having a broad size distribution, larger
agglomerates on the ink-absorbing layer absorb many
ultrafine ink droplets. That is, the ultrafine ink
droplets cannot be held at discharged positions, and

15   bleed from the discharged positions.

b) The above conventional aqueous nanoparticle ceramic
agglomerate dispersion is generally prepared by
dispersing 1 to 50% of nanoparticle ceramic agglomerate
into deionized water using a conventional mixer. When

20   this dispersion is treated using a conventional
ultrasonic homogenizer for a predetermined time, or
using a jet-mill apparatus for a predetermined time in
which ultrahigh-pressure counter jet streams of the
dispersion collide with each other, the nanoparticle

25   ceramic agglomerates are rapidly disintegrated in the
aqueous medium. When the nanoparticle ceramic
agglomerate satisfies the following conditions by
controlling the treatment time, the resulting
nanoparticle ceramic agglomerates in the dispersion have

30   a relatively small and uniform size, an ink-absorbing
layer containing this aqueous nanoparticle ceramic
agglomerate dispersion can hold fine ink droplets at
discharged positions, without bleeding, and an image
printed on an ink-jet recording medium is significantly

35   sharp and clear. That is, the conditions are:

The average diameter of the nanoparticle ceramic
agglomerate dispersed in deionized water is 0.05 to 0.3 μm
according to measurements at a viscosity suitable for

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coating of 10 to 200 mPa·s using a laser diffraction particle size distribution measurement apparatus, and the ratio of the peak width (half width) at a position having a height which is half the maximum height of a curve shown in

5   Fig. 2 of the particle size distribution determined according to the results of the measurement to the maximum height is 0.7 or less.

Accordingly an aqueous nanoparticle ceramic agglomerate dispersion in accordance with the present invention, for

10   forming an ink-absorbing layer of an ink-jet recording medium, comprises a nanoparticle ceramic agglomerate dispersed in deionized water, wherein the nanoparticle ceramic agglomerate has an average diameter of 0.05 to 0.3 µm at a viscosity suitable for coating of 10 to 200 mPa·s

15   as measured by a laser diffraction particle size distribution measurement apparatus, and the ratio of the peak width at a height which is half the maximum height in a size distribution curve of the nanoparticle ceramic agglomerate, determined according to the results of the

20   measurement, to the maximum height is 0.7 or less.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a size distribution curve of ceramic agglomerates in an aqueous nanoparticle ceramic agglomerate dispersion

25   in accordance with the present invention; and

Fig. 2 is a size distribution curve of ceramic agglomerates in a conventional nanoparticle ceramic agglomerate dispersion.

30   **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

In the present invention, the average diameter of the nanoparticle ceramic agglomerate is in a range of 0.05 to 0.3 µm. At an average diameter less than 0.05 µm, there are

no longer distinct differences in the quality of printed images. At a diameter exceeding 0.3 μm, some fine ink droplets of different colors having diameters of 20 μm or less are absorbed in the same nanoparticle ceramic

5 agglomerate, resulting in ink bleeding. Thus, the resulting images are not clear.

The ratio of the half width in the size distribution curve of the nanoparticle ceramic agglomerate to the maximum height is in a range of 0.7 or less. At a half width

10 exceeding 0.7, many ceramic agglomerates having diameters which significantly deviate from the average diameter are present. When an ink-absorbing layer contains these ceramic agglomerates, each of the relatively large agglomerates will absorb different types of color inks, resulting in ink

15 bleeding. As a result, the printed image exhibits color irregularities.

The viscosity suitable for coating of the aqueous nanoparticle ceramic agglomerate dispersion is in a range of 10 to 200 mPa·s. At a viscosity of less than 10 mPa·s,

20 the dispersion is not held on the substrate. At a viscosity exceeding 200 mPa·s, the dispersion cannot be uniformly applied on the substrate.

The aqueous nanoparticle ceramic agglomerate dispersion in accordance with the present invention will now be described

25 with reference to the following Examples.

Using $SiCl_4$, $AlCl_3$, or $TiCl_4$ as raw materials, nanoparticle SiO_2 powder, nanoparticle Al_2O_3 powder, and nanoparticle TiO_2 powder, each having a number average primary particle diameter (hereinafter termed average particle diameter)

30 shown in Table 1, were prepared by gas-phase hydrolysis in a burner containing hydrogen and oxygen. Since these nanoparticle ceramic powders were present as agglomerates, they were disintegrated in a conventional dry disintegrator for a predetermined time, and were added to deionized water

35 in a bead mill while stirring to prepare conventional aqueous nanoparticle ceramic agglomerate dispersions

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(hereinafter termed aqueous ceramic dispersion) 1 to 15, each having a viscosity shown in Table 1.

Each of these aqueous nanoparticle ceramic agglomerate dispersions 1 to 15 was treated in a jet-mill apparatus in

5 which counter jet streams of the dispersion collided with each other at a jet-stream radius of 0.1 mm at the collision position, a jet-stream velocity of 600 m/sec and a flow rate of the jet streams at the nozzles of 15 liter/min. for a predetermined time to disintegrate the

10 nanoparticle ceramic agglomerates. In this manner, aqueous nanoparticle ceramic agglomerate dispersions 1 to 15 in accordance with the present invention (hereinafter termed aqueous ceramic dispersions of the present invention) were prepared.

15 After the conventional aqueous ceramic dispersions 1 to 15 and the aqueous ceramic dispersions 1 to 15 of the present invention were maintained at 22°C for 2 hours, the viscosity of each dispersion was measured at 2.5 rpm using an E-type viscometer (made by Toki Sangyo K.K.). The

20 particle size distribution of the nanoparticle ceramic agglomerate in the dispersion was measured using a laser diffraction particle size distribution measurement apparatus, and the average agglomerate diameter was calculated according to the results. Moreover, a size

25 distribution curve was prepared to determine the ratio of the half width (the width at a position having a height which was half the maximum height of the curve) to the maximum height. These results are shown in Table 1.

To 1000 ml of each dispersion was added 10 to 40 g of

30 cationic polymer, 50 to 100 ml of ethanol, 15 to 30 ml of propanol, 10 to 20 ml of ethyl acetate, 20 to 50 g of polyvinyl alcohol, and 1 to 10 g of boric acid to prepare a coating for forming an ink-absorbing layer. The coating was applied onto a recording surface of water-absorbing paper

35 having a thickness of 200 μm, was rapidly cooled, and was dried by hot air at 50°C for 3 minutes. An ink-jet

recording medium having an 80-μm thick ink-absorbing layer
was thereby prepared.

Yellow, magenta, and cyan solid images were printed onto
the ink-jet recording medium using an ink-jet color printer
5   PM-3300C made by Seiko Epson Corporation, and reflection
densities were measured for monochromatic light of red,
green, and blue. The results are shown in Table 2.

A color image of a person having a size of 250×180 mm was
printed on the ink-jet recording medium and the image
10   quality was observed at a magnification of 3000 using a
high-precision digital microscope.

·Table 1

Type		Average Particle Diameter of Raw Material (nm)	Nanoparticle Ceramic Agglomerate				
			Material	Concentration (%)	Viscosity (mPa·s)	Average Diameter (μm)	Ratio
Aqueous Ceramic Dispersion of Present Invention	1	40	SiO_2	5	10	0.06	0.51
	2	7	SiO_2	30	30	0.08	0.55
	3	12	SiO_2	30	50	0.10	0.60
	4	30	SiO_2	50	100	0.20	0.62
	5	7	SiO_2	50	200	0.29	0.65
	6	13	Ai_2O_3	5	10	0.07	0.55
	7	13	Ai_2O_3	20	30	0.09	0.57
	8	13	Ai_2O_3	30	50	0.16	0.58
	9	10	Ai_2O_3	40	100	0.20	0.61
	10	10	Ai_2O_3	50	200	0.25	0.63
	11	39	TiO_2	5	10	0.05	0.48
	12	21	TiO_2	20	30	0.10	0.58
	13	13	TiO_2	25	50	0.16	0.60
	14	21	TiO_2	35	100	0.21	0.62
	15	13	TiO_2	50	200	0.30	0.66
Conventional Aqueous Ceramic Dispersion	1	40	SiO_2	5	33	1.50	1.10
	2	7	SiO_2	30	95	3.04	1.02
	3	12	SiO_2	30	181	5.20	1.15
	4	30	SiO_2	50	335	10.32	1.32
	5	7	SiO_2	50	841	20.45	1.48
	6	13	Ai_2O_3	5	37	2.02	1.02
	7	13	Ai_2O_3	20	97	5.00	1.11
	8	13	Ai_2O_3	30	169	10.03	1.15
	9	10	Ai_2O_3	40	388	19.12	1.24
	10	10	Ai_2O_3	50	765	29.28	1.44
	11	39	TiO_2	5	30	1.09	1.01
	12	21	TiO_2	20	79	3.00	1.10
	13	13	TiO_2	25	221	10.52	1.22
	14	21	TiO_2	35	398	15.06	1.31
	15	13	TiO_2	50	820	23.04	1.35

Table 2

Type		Image Density		
		Yellow	Magenta	Cyan
Aqueous Ceramic Dispersion of Present Invention	1	2.1	2.1	2.2
	2	2.0	2.1	2.2
	3	2.1	2.1	2.2
	4	2.2	2.2	2.2
	5	2.0	2.2	2.3
	6	1.9	2.0	2.0
	7	1.8	1.9	1.9
	8	1.8	1.9	2.0
	9	1.7	1.8	1.8
	10	1.8	1.8	1.7
	11	1.7	1.9	1.8
	12	1.7	1.8	1.9
	13	1.8	1.8	1.8
	14	1.8	1.8	1.7
	15	1.8	1.7	1.6
Conventional Aqueous Ceramic Dispersion	1	1.6	1.8	1.9
	2	1.5	1.8	1.8
	3	1.4	1.7	1.8
	4	1.8	1.8	1.8
	5	1.7	1.7	1.7
	6	1.6	1.7	1.7
	7	1.6	1.6	1.6
	8	1.5	1.7	1.7
	9	1.5	1.7	1.7
	10	1.5	1.6	1.6
	11	1.6	1.7	1.7
	12	1.7	1.7	1.8
	13	1.6	1.6	1.6
	14	1.5	1.6	1.5
	15	1.4	1.6	1.5

The results in Table 1 demonstrate that the diameters of the agglomerates of the aqueous ceramic dispersions 1 to 15 in accordance with the present invention are smaller and more uniform than those of the conventional aqueous ceramic dispersions 1 to

5   15. Since the ink-absorbing layer formed of one of the aqueous ceramic dispersions 1 to 15 in accordance with the present invention contains relatively fine and uniform agglomerates, ink droplets discharged from the ink-jet printer are precisely maintained at the discharged positions. Thus, the images printed

10 on the ink-jet recording medium have a high density and are significantly clearer.

Accordingly, the aqueous nanoparticle ceramic agglomerate dispersion in accordance with the present invention can provide an ink-jet recording medium which contributes to improvements in

15 performance of ink-jet printers.

Further variations and modifications of the foregoing will be apparent to those skilled in the art and are intended to be encompassed by the claims appended hereto.
Japanese patent application 2000-200794 of July 3, 2000 is relied

20 on and incorporated herein by reference.